(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 451 664 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **91105141.5**

(22) Date of filing: **02.04.91**

(51) Int. Cl.[5]: **D06M 15/431**, D06M 13/285, D06M 15/285, D06M 15/356, D21H 21/34, D21H 25/06

(30) Priority: **12.04.90 GB 9008421**

(43) Date of publication of application: **16.10.91 Bulletin 91/42**

(84) Designated Contracting States: **AT BE CH DE DK ES FR GB GR IT LI LU NL SE**

(71) Applicant: **Albright & Wilson Limited**
210-222 Hagley Road West
Oldbury Warley West Midlands B69 4PR(GB)

(72) Inventor: **Zakikhani, Moshen**
9 Brooklands Drive
Kidderminster(GB)

(74) Representative: **Savidge, Roger Gordon Madgwick et al**
c/o Albright & Wilson Limited, P.O. Box 2098,7 Stars Road
Oldbury, Warley, West Midlands B69 4PR(GB)

(54) **Treatment of fabrics.**

(57) Fabrics, in particular cotton polyester fabrics, are treated with a nitrogen containing polymer (or precursor therefor) and then subsequently treated with a THP compound and cured with heat and/or ammonia, giving higher fire retardance than corresponding fabrics without the pretreatment step.

EP 0 451 664 A1

This invention relates to a fabric treatment process, in particular one rendering fabrics flame retardant with organo phosphorus compounds.

The flame retardant treatment of cotton fabric with tetra kis (hydroxymethyl) phosphonium compounds (hereafter called THP compounds) or precondensates thereof with urea has been described in USP2983623, 4068026, 4078101, 4145463 and 4494951. The treatment processes involved impregnation of the fabric with an aqueous solution of the chemicals, followed by drying, treatment with ammonia to cure the phosphorus compounds in order to insolubilize the phosphorus onto the fabric, finally with oxidation and washing to leave a treated fabric whose flame resistance is retained even after many washes in use.

However the cure efficiency which is a measure of the effectiveness of the cure in insolubilizing the phosphorus on the fabric, is not always ideal and a percentage of the expensive phosphorus chemicals applied in the impregnation step is not cured and is washed off the fabric after the cure and wasted. The cure efficiency for cotton fabrics is higher than for cotton polyester fabrics and especially polyester cotton fabrics and in some cases adequate fire retardant properties cannot be provided to the latter with THP compounds. Furthermore, while some techniques enable the necessary fire retardant properties to be provided to the fabric when first cured, those properties often diminish significantly on repeated washing.

We have discovered a process which can increase the amount of P compound fixed on the substrate especially ones comprising non cellulosic fibres, and can enable adequate fire retardant properties to be provided for fabrics comprising non cellulosic fibres such as cotton polyester blends.

The present invention provides a process for the flame retardant treatment of an organic fibrous substrate containing reactive groups, which process comprises impregnating said substrate with a nitrogen containing polymer (or precursor therefor) and with an aqueous solution of an organophosphorus compound, to provide an impregnated substrate which is dried and cured, to give a cured substrate.

The nitrogen containing polymer may be applied to the substrate at the same time as the organophosphorus compound, but preferably the polymer or precursor is applied in a first step to give a first impregnated substrate and then the organophosphorus compound is applied in a second step. The first impregnated substrate is usually maintained to allow the polymer to interact with the substrate before the second step.

The nitrogen containing polymer is preferably free of P atoms and may be capable of reaction with cellulose on heating eg at 150°C. It is preferably a polyelectrolyte containing a plurality of N atoms (especially in tertiary or quaternary form), which may interrupt a carbon polymeric chain, but preferably are in groups pendant from a hydrocarbon polymeric chain. The hydrocarbon polymer backbone is preferably made of structural units derived from mono or di ethylenically unsaturated compounds containing one or more N atoms. Examples of mono ethylenically unsaturated compounds are vinyl compounds with a heterocyclic N ring, (such as N- vinyl pyridine, N-vinylpyrrolidine, N-vinyl pyrrolidone and their C-ring alkyl derivatives), and also acrylic and methacrylic compounds with amide or amine groups such as acrylamide, methacrylamide, ammonium acrylate and methacrylate, and their mono, di, tri or tetra N-alkyl derivatives, especially those in which the alkyl group contains 1-6 carbon atoms (such as methyl or ethyl). The polymer may be a homo or copolymer of monomers, each of which contains the N atom or atoms, or may be a copolymer with other N- free ethylenically unsaturated monomers such as acrylic or methacrylic acid or corresponding esters, eg with alkanols of 1-6 carbon atoms.

The weight proportion of N containing monomers to N-free monomers is usually 50-100:50-0 (eg 70-90:30-10), but especially 80-100:20-0, such as 80-95:20-5. Examples of the di ethylenically unsaturated compounds are di allyl amines, especially quaternized di allylamine (such as N,N -dialkyl-N, N-diallyl ammonium halides), in which each alkyl group contains 1-6 carbon atoms such as ethyl, isopropyl, propyl or butyl but especially methyl. Examples of copolymers are those of acrylic acid and acrylamide, and acrylamide and dialkyl diallyl ammonium chloride. Polymeric dialkyl diallyl ammonium chlorides may be made as described in USP 3472740, the disclosure of which is hereby incorporated by reference. Otherwise the polymers from ethylenically unsaturated compounds may be made by conventional means, such as free radical polymerization, especially in aqueous solution or aqueous emulsion.

The nitrogen containing polymer may also contain the N atom in the polymeric backbone and may be made by polymerization involving a ring opening operation (such as the known polymerization of ethylene imine to give polyethylene imine).

The average molecular weight of the nitrogen containing polymer is usually 10000 - 5 million eg (100000 - 3 million), and it is water soluble, (eg with a solubility in water at 20°C of at least 10g/l) or water dispersible.

Other nitrogen containing polymers which may be used are water soluble or water dispersible ones made by condensation polymerization and capable of further condensation with cellulose, such as polyamines, polyamides and polyamine/polyamide epichlorohydrin reaction products.

A precursor capable of forming the nitrogen containing polymer on heating may be used, in particular a monomer which can be polymerized to form the polymer, eg in situ in the fabric during a drying or dwell time either after one step or after two step impregnation or between impregnations in a two step impregnation (as before herein described), or especially during any heat cure.

Particularly useful monomers are di ethylenically unsaturated compounds, such as the di allylamine salts mentioned above. The monomer may also react with the substrate or the organophosphorus compound rather than polymerizing to polymer which itself interacts. The precursor is preferably added in a first step separate from the organophosphorus treatment.

The organic fibrous substrate is especially one comprising or consisting essentially of cellulosic fibres. The cellulosic fibres are preferably natural cotton, but may be ramie, flax, paper or cardboard or regenerated fibres (e.g. viscose or cuprammonium fibres) or partly etherified or esterified cellulose (e.g. cellulose acetate or propionate). The substrate may be substantially completely cellulosic eg 100% cotton or may contain both cellulosic and non cellulosic organic fibres, or just contain non cellulosic organic fibres eg 100% polyester fibres. Inorganic fibres such as glass fibres are usually absent.

The non cellulosic fibres are preferably polyester or polyamide fibres but may also be acrylic. The polyamide may be an aliphatic one, such as copolymers of a polyamine (such as a diamine) preferably an alkylene diamine, eg of 4-12 carbon atoms and a poly carboxylic acid eg a dicarboxylic acid, of 4-14 carbon atoms such as an alkylene dicarboxylic acid (e.g. Nylon 66), or polylactams such as Nylon 6. Alternatively the polyamide may be an aromatic one, such as aramids based on aromatic dicarboxylic acids and phenylene diamines. The acrylic polymer may be polyacrylonitrile homopolymer or copolymer with vinyl chloride, as in modacrylic fibres. The substrate can contain at least 20% of cellulosic fibres and up to 80% of coblendable fibres e.g. 10-80% especially 25-80% of coblendable fibres such as polyamides. However preferably the substrate comprises cellulosic fibres and polyester fibres. The substrate usually contains up to 80% (e.g up to 70%) polyester fibres and from 20% (e.g. from 30%) upwards of cellulosic fibres, e.g. 1-80% or 1-70%, such as 15-70% particularly 22-38% or 45-75% polyester fibres and 20-99% or 30-99% (such as 30-85%), particularly 62-78% or 25-55% cellulosic fibres.

Substrates comprising at least 45% non cellulosic fibres, eg polyester fibres such as 45-100% polyester, are preferred as are ones comprising 30-78% cellulosic fibres and 22-70% polyester fibres, or 30-62% cellulosic fibres and 38-70% polyester fibres. The polyester is usually a condensation product containing structural units from an aliphatic alcohol, e.g. dihydric alcohol, especially ethylene glycol or butane diol (or mixtures thereof) and an aromatic dicarboxylic acid, e.g. terephthalic acid, or a mixture thereof with other dicarboxylic acids, such as isophthalic acid, or sebacic acid.

If desired, the fibrous substrate may be one of the above non cellulosic ones having groups capable of interaction with the cationic compound. Thus the substrate may be a polyester, with the cationic polymer interacting with hydroxyl groups, or a polyamide with the cationic polymer interacting with carboxyl or a polyacrylonitrile, with interaction of the cationic polymer with nitrile groups. The polyester may be described above, while the polyamide may be a reaction product of a polyamine, e.g. a diamine, e.g. 4-12 carbons, with a polyarboxylic acid, e.g. a dicarboxylic acid of 4-14 carbon atoms. The polyacrylonitrile may be a homopolymer or copolymer with vinyl chloride as in modacrylic fibres.

The substrate fibres may be in the form of thread or non woven fabric, but are preferably as woven fabric. Mixtures of fibres e.g. of cellulosic and other fibres may be an intimate or non intimate mixture, but the fibres are preferably in the form of blend of cellulosic fibres and the other fibres, e.g. polyester fibres, as in cospun blends such as cotton polyester or polyester cotton staple fibre, but may be in the form of core spun yarn with a core of the other fibre, e.g. polyester sheathed in cotton fibres. In a fabric, the warp and weft fibres are preferably the same, but may be different, e.g. one may be from cotton fibres and the other from e.g. polyester cotton fibres. Thus in this specification the term "blend" also includes unions and union/blends as well as core sheath fibres. The substrate is preferably a fabric with a weight of 0.05-1.0kg/m^2 (e.g. 0.150-0.40kg/m^2) or 0.05-0.20kg/m^2, such as polyester cotton shirting or sheeting or curtain fabric.

The nitrogen containing polymer (or precursor) is usually applied in aqueous solution or dispersion, e.g. of 0.1-30% (such as 0.2-15%), especially 0.5-4% w/w and at pH 2-9 eg. 2-4. The weight of nitrogen containing polymer (or precursor) applied is usually 0.01-20% (e.g. 0.1-10%), especially 0.5-5% based on the weight of the untreated fabric. The nitrogen containing polymer (or precursor) may be impregnated into the fabric with a wet pick up of 50-150% and then, after initial drying if desired (e.g. with the impregnated fabric heated at 80-100°c for 0.1-5 minutes), the impregnated fabric is then treated by heating at 90-150°C (e.g. 90-130°C) for 0.5-10 minutes (e.g. 1-5 minutes). Instead of the heating step, the impregnated fabric may be kept, e.g at ambient temperature for 10-60 hours (e.g 10-30 hours) preferably while being allowed to dry. If desired the polymer (or precursor) may be applied with a minimum add-on technique to provide a

10-50% wet pick up; thereafter the fabric may be dried or kept with a dwell time of eg 0.2-24 hours before the second step. A foam minimum add on technique may be used, with a cationic or amphoteric foaming agent and a stabilizer. In this treatment or fixing step the nitrogen containing polymer is believed to interact with the substrate, especially hydroxyl, amide or ester groups thereon, to give a treated substrate having the cationic polymer bound or attracted thereto by ionic bonds.

In the preferred form of the process, after the treatment with the nitrogen-containing-polymer, the substantially dry substrate is then treated with the organophosphorus compound. In the tetrakis - (hydroxyorgano) phosphonium compound, each hydroxyorgano group is preferably an alpha-hydroxyorgano group of 1-9 carbons. Especially said alpha-(hydroxyorgano) group is one of formula $\overline{\text{HOC-}}$ (R^1R^2), wherein each of R^1 and R^2 (these being the same or different) represents hydrogen or an alkyl group of 1 to 4 carbons, e.g. methyl, or ethyl. Preferably R^1 is hydrogen, and R^2 is methyl or especially hydrogen, as in tetrakis (hydroxymethyl) phosphonium (THP) compounds. The use of tetrakis hydroxyorgano phosphonium compounds in general will hereafter be exemplified with respect to THP compounds with - corresponding molar amounts of the other compounds used instead of the THP compound.

The substrate is treated with an impregnation solution which is an aqueous solution of a THP salt mixed with a nitrogen compound condensable therewith to form a water soluble precondensate, or a solution of a precondensate of said salt and nitrogen compound, or a solution of THP salt, or water soluble self-condensate thereof, or at least partly neutralised THP salt, (e.g. THP hydroxide), with or without the nitrogen compound. The impregnation solution may alternatively comprise a solution of said precondensate and further nitrogen compound (eg urea), as in a solution with a molar ratio of total nitrogen compound (free and combined) to THP group (free and combined) of 0.8-2:1, eg 0.8-1.5:1. The nitrogen compound is preferably one with at least two NH groups (such as 2-4), but advantageously contains two NH or especially two NH_2 groups. The nitrogen compound is usually bifunctional and may be an amine but is especially an amide. Examples of suitable nitrogen compounds are biuret, guanidine, melamine and methylolated melamines, but urea is the preferred species for the purposes of this invention, especially in the absence of melamine or a methylolated melamine. The nitrogen compound is preferably urea whenever it is present in the precondensate.

In a preferred embodiment of this invention, the solution contains a precondensate of THP salt, e.g. chloride or sulphate, and the nitrogen compound in a molar ratio of nitrogen compound to THP of 0.05-0.8:1, e.g. 0.05-0.6:1, or 0.22-0.8:1, such as 0.25-0.6:1, especially 0.4-0.6:1. The pH of said solution is usually 2-7.5, such as 4-6.5, e.g. 4-5. The atom ratio of total N atoms in the nitrogen compound or condensate to the total P atoms from THP salt or condensate in the impregnation solution is usually not greater than 4:1, eg 1-3:1.

The concentration of organophosphorus compound in the aqueous solution may be 5-70% eg 5-35% or 35-70% (expressed by weight as THP^+ ion), but is preferably 20-35%.

If desired the solution may contain a wetting agent such as a nonionic one, eg in amount of 0.05-0.5% by weight of the impregnation solution, a fabric softener such as a polyethylene one and in preferred amount of 0.1-2% by weight, and a salt of a strong acid and weak base (such as an ammonium or alkaline earth metal chloride or nitrate or ammonium acid phosphate) as catalyst for the heat cure, and in amount of 0.1-5% by weight.

The treated substrate is impregnated to give an organo phosphorus pick up of less than 40% e.g. 10-40%, (such as 10-30%) especially 20-30% (as THP ion based on the original weight of the substrate). The substrate can be impregnated with solution and the wet substrate e.g. fabric usually squeezed to a wet pick up of 50-130%, e.g. 60-100% (based on the original weight of the substrate). Alternatively the treated substrate may be impregnated with a concentrated impregnation solution via a minimum add-on, eg foam, technique and a 10-50% wet pick up.

The organophosphorus impregnated substrate is then dried, e.g. to a moisture content of 0-20%, e.g. 5-15% such as about 10%, for subsequent ammonia cure and to substantial dryness for subsequent heat cure (the percentage being derived from the increase in weight of the fabric and the weight of chemicals impregnated). The drying may be in a stenter oven or over heated cans e.g. steam cans, and may involve heating at 80-160 °C for 10 min to 10 secs e.g. at 100-120 °C for 3min to 30 secs . The dried substrate is then cured. The cure may be by treatment with ammonia, usually gaseous ammonia, which diffuses through the substrate and/or is forced through the substrate, e.g. by passage of the fabric over a perforated tube through which ammonia has is emitted. Examples of apparatus and techniques suitable for the ammonia cure are given in USP 4145463, 4068026 and 4494951, the disclosure of which is hereby incorporated by reference. Alternatively or preferably prior to the ammonia cure, the dried organophosphorus impregnated substrate may be heat cured, e.g. at a temperature of at least 100 °C (such as 100-200 °C) or 100-180 °C (such as 130-170 °C) for 10-0.5 minutes e.g. 7-1 minutes.

Higher temperatures with long curing times should be avoided with substrates containing at least a majority of cellulosic fibres, especially 100% cotton. While the dried substrate may then be heat cured, preferably the drying and heat curing steps are combined with just heating under the heat cure conditions. When a heat cured fabric is subseqently to be cured with ammonia, the heat cured fabric is preferably submitted to a humidity equilibration step to allow the fabric to recover its moisture content before the ammoniation.

The cured substrate usually has a solids add-on (derived from the organo phosphorus impregnation and cure stages) of 10-50%, or 10-40%, (e.g. 10-30%) such as 10-25% or 15-30%, especially 20-30%, (by weight of the original substrate), based on a total organophosphorus compound pick up of 16-36%, e.g. 20-28% (expressed as THP ion on the same basis).

The cured substrate is then usually subjected to at least one of the following operations: further insolubilization of the cured resin in the treated substrate, oxidation in order to convert at least some trivalent phosphorus to pentavalent phosphorus in the cured resin, or washing with aqueous base and washing with water. The oxidation is preferably by contact with an aqueous solution of an oxidising agent, preferably a peroxy compound, such as aqueous hydrogen peroxide solution e.g. of 0.5-15% concentration, such as 1-5% strength, or sodium perborate solution, e.g. of 1-10% concentration, usually applied in excess, and usually for 0.1-10 mins at 0-40 °C. Alternatively the oxidation may be performed with a gas containing molecular oxygen, preferably air, and particularly with the gas being drawn or blown through the substrate. Thus the substrate in the form of fabric can be passed over a vacuum slot or perforated tube though which the gas is blown or sucked.

After the oxidation, or instead thereof, the cured substrate may be washed with an aqueous medium, preferably an aqueous solution of base, e.g. sodium carbonate solution and/or rinsed with water. The oxidation preferably reduces the residual content of formaldehyde on the cured substrate.

Alternatively the cured substrate may simply be rinsed with water or submitted to other operations to reduce its content of water soluble materials. Finally the cured fabric is dried, to give a final substrate.

The final substrate e.g. fabric can be used for making workwear such as overalls, boiler suits and protective clothing including uniforms, particularly from 30-70% e.g. 55-70% cotton and 70-30% e.g. 45-30% polyester, and household fabrics such as sheets and curtains particularly from 30-70% e.g. 30-60% cotton and 40-70% polyester.

If the process of the invention is compared to the corresponding one without the nitrogen containing polymer (or precursor) step, the initial uptake of THP compound by the substrate in the impregnation may be increased, the cure efficiency may be increased and the loss of cured P compound from the final substrate during washing in use may be reduced. Thus for a constant total weight phosphorus chemical applied to the substrate, the cured substrate of the invention usually has a higher percentage of bound phosphorus and may also have a better handle than the corresponding cured substrate without the initial treatment with the nitrogen containing polymer. There is thus less wastage of phosphorus chemical. The flame retardant properties e.g the char length, are usually improved enabling fabrics to pass more severe flammability tests than without the treatment with nitrogen containing polymer (or precursor).

The final substrate obtained by the process of the invention may also have enough cured and bound phosphorus containing-resin to enable it to reach the exacting flame retardancy standards e.g. BS6249 Part 1 1984 Part B, which may not be passed by the same original substrate cured without the initial treatment with nitrogen containing polymer (or precursor). The final substrate obtained by the process of the invention may also have less reduction in strength compared to corresponding substrates without the initial treatment.

In this specification, unless otherwise noted parts and percentages are by weight.

The invention is illustrated in the following Examples in which all the fabrics had been previously submitted to a desizing treatment.

Example 1

An aqueous dispersion of poly (dimethyl diallyl ammonium chloride) was obtained by a reaction in which into a reactor with stirrer and condenser were added toluene (50g) and a nonionic surfactant (15g) and the reactor heated to 80 °C followed by simultaneous addition of an aqueous solution of dimethyl diallyl ammonium chloride (50g) in water (50g) and di-(4 tert butylcyclohexyl) peroxydicarbonate (0. 15g). The reactor contents were stirred at 80 °C for 3 hours to leave an emulsion, which was then heated to remove the toluene by distillation with water, with addition of extra water in lieu of the toluene and water distilled. The product was a stable aqueous dispersion of the average molecular weight of the polymer was about 1 million.

(a) A 67:33 intimate blend polyester cotton fabric of 0.246kg/m^2 was impregnated with a 2% w/w

aqueous dispersion of the above polymeric dimethyl diallyl ammonium chloride. The excess of liquid was then separated from the fabric, which was allowed to dry at room temperature overnight to leave a treated fabric comprising about 1.6% of the polymer.

(b) The treated fabric was then impregnated with an aqueous solution of 1:2 molar condensate of urea and tetrakis (hydroxy methyl) phosphonium chloride containing 25.2% solids (expressed by weight as THP^+ ion and the excess of liquid squeezed from the fabric.

(c) The fabric was then heat cured at 150° C for 3 minutes, and then its water content returned to normal by equilibration in a humidity controlled room overnight. The heat cured fabric was then cured further with ammonia gas which was passed through the fabric in a chamber as described in USP 4145463.

(d) After the ammonia cure, the fabric was washed with 10% hydrogen peroxide solution, rinsed with water, washed with aqueous sodium carbonate and then rerinsed and dried, to give a final fabric.

The final fabric was then analysed for P and N; it was also tested for flame retardancy before and after washing 40 times at 93° C, the washing being as in the manner described in DIN 53920 procedure 1 with soft water. The test method used was according to BS 5438 (1989) Test 2A. In all cases the fabrics passed the flammability requirements of BS 6249 Index B. The analysis results were as follows:

FABRIC	%P	%N
Cured (step c)	1.94	1.56
Final fabric (step d)	1.81	1.65

The fabric passed the ignition test even after the 40 washes.

Example 2

The process of Ex 1 was repeated with a different fabric, namely a 60:40 cotton/polyester intimate blend fabric of weight 0.268kg/m², and with a different pretreatment agent, namely monomeric di (allyl) di (methyl) ammonium chloride added in 2%, 5% or 10% aqueous concentration to give a wet pick up of about 70-90%. The flammability, % P and %N analyses were done on the final fabric as such and after 20 washes. The results were as follows.

% Agent in solution	Final Fabric %P	Final Fabric %N	Final Fabric Char length mm	Fabric after 20 washes %P	Fabric after 20 washes N%	Fabric after 20 washes Char Length mm
2	3.05	3.05	60	2.63	2.40	50
5	2.9	2.90	54	2.43	2.24	47
10	2.98	2.90	58	2.38	2.19	42

Examples 3 - 9

The process of Ex 1 was repeated with two different polymeric nitrogen compounds, namely (Ex 3-6) a water soluble copolymer of acrylamide and acrylic acid in about 90:10 ratio and (Ex7-9) a water soluble

polyethylene imine. The final fabrics and those after 20 washes were tested for flammability. All passed the flammability tests the results of these on the final fabrics being as follows.

Example	% polymer in solution in step (a)	Char length mm
3	1	81
4	2	76
5	5	79
6	10	75
7	0.5	90
8	1.5	85
9	2	87

Claims

1. A process for the flame-retardant of an organic fibrous substrate containing reactive groups, said process characterised by:
   (a) impregnating the substrate with a nitrogen containing polymer, or precursor therefor, and with an aqueous solution of an organophosphorus compound,
   (b) drying the substrate,
   (c) curing the substrate by heating at a temperature of at least 100 C and/or treating with ammonia.

2. A process according to Claim 1, **characterised in that** the organophosphorus compound is applied to the substantially dry substrate after the impregnation thereof with the nitrogen containing polymer, or precursor therefor.

3. A process according to Claim 1 or 2, **characterised in that** the organic fibrous substrate consists essentially of cellulosic fibres, e.g. natural cotton, ramie, flax, paper of cardboard, viscose or cuprammonium fibres, or cellulose acetate or propionate.

4. A process according to Claim 1 or 2, **characterised in that** the organic fibrous substrate comprises cellulosic and non-cellulosic, e.g. polyester, polyamide or polyacrylonitrile fibres.

5. A process according to Claim 1 or 2, **characterised in that** the organic fibrous substrate consists essentially of non-cellulosic fibres.

6. A process according to any one of Claims 1 to 5, **characterised in that** said nitrogen containing polymer is a homopolymeric or copolymeric polyelectrolyte containing a plurality of N atoms, which may interrupt a carbon polymeric chain or be in groups pendant from a hydrocarbon polymeric chain, especially where said nitrogen containing polymer is free of phosphorus atoms, especially where said nitrogen containing polymer comprises a hydrocarbon polymer backbone itself comprising structural units derived from mono ethylenically unsaturated compounds containing one of more N atoms, e.g. N-vinyl pyridine, N-vinylpyrrolidine, N-vinyl pyrrolidone and their C-ring alkyl derivatives, or acrylamide, methacrylamide, ammonium acrylate and methacrylate, the their mono, di, tri or tetra N-methyl or N-ethyl derivatives, or structured units derived from diethylenenically unsaturated compounds containing one or more N-atoms, especially where said diethylenically unsaturated compounds are quaternised di allykamine in which each alkyl group contains 1 to 6 carbon atoms, especially where said nitrogen containing polymer is a homopolymer of dialkyl diallyl ammonium chloride, or a copolymer of

acrylamide and dialkyl diallyl ammonium chloride.

7. A process according to any one of Claims 1 to 5, **characterised in that** the nitrogen containing polymer comprises a hydrocarbon polymer backbone, itself also comprising nitrogen free ethylenically unsaturated monomers, e.g. acrylic or methacrylic acid or corresponding esters with alkanols of 1-6 carbons atoms, especially where the weight proportion of nitrogen containing monomers to nitrogen-free monomers within said nitrogen containing polymer 50:50 to 100:0, especially where said weight proportion is from 80:20 to 100:0, especially where said nitrogen containing polymer is a copolymer of acrylic acid and acrylamide.

8. A process according to any one of Claims 1 to 5, **characterised in that** the nitrogen containing polymer also contains the nitrogen atom in the polymer backbone, e.g. where said nitrogen containing polymer is polyethylene.

9. A process according to any one of Claims 1 to 5, **characterised in that** the nitrogen containing polymer is made by condensation polymerisation, and in that said nitrogen containing polymer is capable of further condensation with cellulose, e.g. where said nitrogen containing polymer is a polyamine, polyamide or a polyamine/polyamide epichlonohydrin reaction product.

10. A process according to any one of Claims 1 to 9, **characterised in that** the nitrogen containing polymer has an average molecular weight of 1000 to 5 million, and in that said nitrogen containing polymer is water soluble or water dispersible, and in that said nitrogen containing polymer, or precursor therefor, is applied, to the substrate, in the impregnation (a) thereof, in aqueous solution or dispersion, especially where the concentration of said aqueous solution or dispersion is from 0.1 to 30% w/w, and in that the weight of nitrogen containing polymer, or precursor therefor, applied thereby is from 0.01 to 20% based on the weight of the untreated fabric.

11. A process according to any one of Claims 1 to 10, **characterised in that** the impregnation (a) is achieved by treating said substrate with a solution comprising a nitrogen-containing polymer, or precursor therefor, e.g. a diallylamine salt, such that the wet pick-up is from 50 to 150%, especially where the impregnated substrate is then subjected to one or more of the following treatments:
(i) drying by means of heating at 80 to 100 C for 0.1 to 5 minutes.
(ii) heating at 90 to 150 C for 0.5 to 10 minutes.
(iii) keeping at ambient temperature for 10 to 60 hours, especially where said impregnated substrate is concomitantly allowed to dry.

12. A process according to any one of Claims 1 to 10, **characterised in that** the nitrogen-containing polymer, or precursor therefor, e.g. a diallylamine salt, is applied to the substrate, in the impregnation (a) thereof, via a minimum add-on technique, especially where said minimum add-on technique is a foaming technique, using a cationic or amphoteric foaming agent and a stabiliser, and in that the wet pick-up is 10 to 50%.

13. A process according to any one of Claims 1 to 12, **characterised in that** the impregnation (a) is achieved with a tetrakis -(hydroxyorgano) phosphonium compound, especially where said hydroxyorgano group is an alpha - hydroxyorgano group of 1 to 9 carbons, especially where said alpha - hydroxyorgano group is of general formula HO-C(R^1R^2), wherein R^1 and R^2, which are the same or different, are hydrogen or an alkyl group of 1 to 4 carbons, especially a tetrakis (hydroxymethyl) phosphonium (THP) compound, or a water-soluble self-condensate thereof, or a water-soluble condensate thereof with an organic nitrogen compound, e.g. urea, biuret, guanidine, melamine or methylolated melamine, or a mixture of said organic nitrogen compound with phosphonium compound or condensate or self-condensate.

14. A process according to any one of Claims 1 to 13, **characterised in that** the impregnation (a) is achieved by means of a solution comprising a precondensate of THP salt and organic nitrogen compound such that the molar ratio of organic nitrogen compound to THP therein is from 0.05:1 to 0.8:1, especially from 0.25:1 to 0.6:1, especially from 0.4:1 to 0.6:1, and in that said solution has a pH of from 2 to 7.5, especially from 4 to 5, and in that the concentration of organophosphorus compound (by weight expressed as THP^+ ion) in said impregnation solution is from 5 to 70%, impregnation

solution also comprise one or more of the following additives:

(i) a wetting agent, especially where said wetting agent is non-ionic and especially where said wetting agent is present in an amount of from 0.05 to 0.5% by weight of said impregnation solution,

(ii) a fabric softener, especially where said fabric softener is present in an amount of from 0.1 to 2% by weight of said impregnation solution,

(iii) a catalyst, especially where said catalyst comprises a salt of a strong acid and a weak base, e.g. an ammonium or alkaline earth metal chloride or nitrate or an ammonium acid phosphate, and especially where said catalyst is present in an amount of from 0.1 to 5% by weight of said impregnation solution.

15. A process according to any one of Claims 1 to 14, **characterised in that** the impregnation (a) is achieved by treating said substrate with said impregnation solution to give an organophosphorus pick -up of less than 40% (as THP^+ ion based on the original weight of the said substrate), especially from 20 to 30% (as THP^+ ion based on the original weight of said substrate).

16. A process according to Claim 15, **characterised in that** the wet substrate is squeezed to a wet pick-up of from 50 to 130% (by weight based on the original weight of said substrate).

17. A process according to any one of Claims 1 to 14, **characterised in that** the treated substrate is impregnated with a concentrated impregnation solution via a minimum add-on technique, especially a foaming technique, and in that the wet pick-up is from 10 to 50% (by weight based on the original weight of said substrate).

18. A process according to any one of Claims 1 to 17, **characterised in that** the heat curing of (c) takes place in a stetner or baking oven at a temperature of form 100 to 180 C, and in that the curing time is from 10 to 0.5 minutes.

19. A process according to Claim 18, **characterised in that** said heat curing takes place prior to curing with ammonia.

20. A process according to any one of Claims 1 to 19, **characterised in that** the cured substrate is subjected to at least one of the following operations:

(i) further insolubilisation of the cured resin in the treated substrate;

(ii) oxidation;

(iii) washing with aqueous base and washing with water and in that said oxidation (ii) is achieved by application of an oxidising agent in excess for from 0.1 to 10 minutes at from 0 to 40 C, and in that said oxidising agent is an aqueous hydrogen peroxide solution of concentration from 0.5 to 15% w/w or an aqueous sodium perborate solution of concentration from 1 to 10% w/w, or in that the cured substrate is subjected to oxidation by means of a gas containing molecular oxygen being drawn or blown through the substrate.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 5141

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-3 958 932 (STANLEY P. ROWLAND ET AL) * column 3, lines 30 - 34 * * column 4, lines 18 - 39 @ column 3, lines 51 - 59 @ column 6, lines 7 - 15 @ columns 6 -14; claims *	1,3-11, 13-16,18	D 06 M 15/431 D 06 M 13/285 D 06 M 15/285 D 06 M 15/356 D 21 H 21/34 D 21 H 25/06
A	FR-A-2 130 501 (TOYO BOSEKI) * the whole document *	1	
X	GB-A-8 847 85 (BRADFORD DYERS'ASS.) * pages 1 - 6 *	1-3,10, 11,13-16, 18	
X	US-A-3 421 923 (CH.GUTH ET AL) * the whole document *	1-3,10, 11,13-16, 18-20	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D 06 M

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	05 July 91	BLAS V.M.

CATEGORY OF CITED DOCUMENTS

- X: particularly relevant if taken alone
- Y: particularly relevant if combined with another document of the same catagory
- A: technological background
- O: non-written disclosure
- P: intermediate document
- T: theory or principle underlying the invention
- E: earlier patent document, but published on, or after the filing date
- D: document cited in the application
- L: document cited for other reasons
- &: member of the same patent family, corresponding document